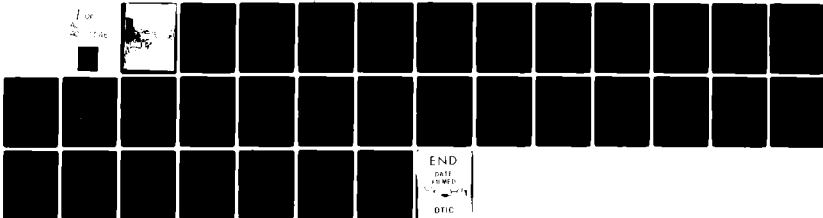


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<p>Advances in our knowledge of the influence of environment on fatigue properties in recent years are reviewed. Much of this has occurred as a result of increased activity in development of water and gas nuclear reactors, heat transfer systems, and offshore structures. Effects of both aqueous and gaseous environments on crack initiation and propagation as well as fatigue life in principally steels, aluminum alloys, and titanium alloys are discussed including the role of environmental factors such as electrochemical potential, solution chemistry, gaseous species, and temperature. Mechanical factors such as frequency and loading waveform are also important in the response of material behavior to environment.</p>														

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ENVIRONMENTAL EFFECTS ON FATIGUE BEHAVIOR OF METALS

INTRODUCTION

The role of environment in fatigue behavior has received a great deal of attention in the past decade. While it has been known for a great many years that the environment can significantly affect fatigue properties, only in recent years has this fact been considered generally by designers and engineers in the development of components and structures. Thus one could say that the most notable advance in the area of environmental effects in the past decade has been its movement from the stage of academic interest to the level of engineering concern.

Impetus for the increased activity in this field was the need for improved operational and structural reliability of advanced energy systems, such as water-cooled, liquid metal and gas-cooled nuclear reactors, heat transfer systems, bridges, and offshore structures. Consequently, environments of interest have included both liquids, such as water, seawater, and liquid metals, and gases, such as hydrogen, water vapor, helium coolant, oxygen, as well as air. Studies of environmental effects have been made over a wide range of temperatures but this review shall be limited to behavior below the creep range. Most of the work has been done on low strength as well as high strength steels, aluminum alloys, and titanium alloys.

Early investigations of environmental effects were on traditional fatigue behavior resulting in S-N curves but with the advent of fracture mechanics methodology crack propagation received attention. Thus as with general fatigue behavior, environmental effects on both crack initiation and propagation were examined. However, the effort on crack initiation has been less because of the experimental difficulties involved, and the findings have been less clear, particularly with respect to gaseous environments. An inherent problem here in the analysis is the distinction between crack nucleation and the early growth stage.

Generally fatigue cracks are surface initiated and the environment acts on the material through the surface. Character of the surface, chemical and diffusion processes, as well as interactions of chemical, mechanical, and adsorption processes are important. Investigations of environmental effects have included the examination of many environmental variables, such as partial pressure of gas, electrochemical potential, solution chemistry, and temperature, and mechanical variables, such as frequency, stress ratio and loading waveform. The combined action of aggressive environment and cyclic stresses is commonly termed corrosion fatigue. Both liquid and gaseous environments generally cause a reduction in fatigue life in metals and alloys through interactions of chemical and mechanical processes at surfaces including crack tips.

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The growing recognition of corrosion fatigue failures in service has altered traditional design considerations and now efforts are being made to include corrosion fatigue data in design codes [1]. Also in this regard, predictive criteria are receiving attention.

Recent advances in our knowledge and understanding of environmental effects on fatigue have been with respect to aqueous solutions including salt water and high temperature water and gases, particularly air, hydrogen, and water vapor and these will all be discussed separately in the following sections. The results obtained in the past decade are emphasized although some significant work from earlier years is also included to provide continuity.

LIQUIDS

Water

Corrosion fatigue behavior in aqueous environments is often for convenience separated into two categories [2,3] according to whether it takes place below or above K_{ISCC} , defined as the stress intensity below which crack growth does not occur in statically loaded material in an aggressive environment. It should be noted however that almost all materials are susceptible to corrosion fatigue but not all exhibit stress corrosion cracking (SCC) and thus corrosion fatigue is not confined to SCC susceptible material. Corrosion may accelerate fatigue and also fatigue may accelerate corrosion. The influence of aqueous environments on behavior is usually ascertained by making comparisons with behavior in air, however it should be noted that air itself is an aggressive environment for most metals compared to vacuum.

Behavior above K_{ISCC} may be controlled by either SCC or fatigue and models based on superposition of these two effects [4,5] have been proposed. In this regime, SCC dominates at low frequencies and fatigue dominates at high frequencies. The approach has met some success with steels but it appears that the superposition model is inadequate for corrosion fatigue of aluminum alloys with the possibility that synergistic interactions are involved. Below K_{ISCC} the environment may enhance fatigue but the superposition approach is of course not applicable.

There is general agreement that aqueous environments affect crack initiation, unlike the uncertain situation with respect to gases. The role of the environment in the initiation stage however is not clear and as reported by Laird and Duquette [6] may involve several processes: pitting, preferential anodic dissolution, protective film rupture, and surface energy reduction by adsorption. No one of these appears to explain all observed corrosion fatigue failures. The dominant process may differ according to material and environment.

In corrosion fatigue, cracks can initiate at the surface either intergranularly or transgranularly. Intergranular corrosion could provide initiation sites at the surface for fatigue cracks which could then grow transgranularly [7]. On the other hand, initiation could be transgranular when slip intersects the surface and fresh slip steps contact the solution, resulting in dissolution of metal atoms [8]. Localized corrosion at slip steps would then lead to formation of cracks. Many small surface cracks could be generated by either process and these could connect and grow. An analysis of how very small distributed cracks could lead to fracture has been made by Kitagawa, et al. [9].

Plastic deformation at the surface differs from that in the interior and the possible consequence of this on initiation has been discussed by several authors [10,11]. Kramer and Kumar [10] state that the surface layer stress is increased under corrosion environments and the relaxation rate is reduced. The changes in the stress state of the surface layer or surface plastic resistance are related to the effect of environment on initiation and propagation. Also Uhlig [12] has proposed that corrosion above a critical rate induces or accelerates plastic flow of the stressed metal and in turn promotes formation of microscopic intrusions and extrusions leading to cracking.

Sensitivity of fatigue to environment varies appreciably for different metal-environment systems and even for different microstructural conditions in the same alloy. For example, the decrease in fatigue strength of a high strength steel produced by an aqueous environment is appreciably larger if the steel is tempered below 400°C [13]. This larger effect is attributed to an increased sensitivity to hydrogen embrittlement.

Among the variables that affect corrosion fatigue the most important are strain range, stress waveform, cyclic frequency, temperature, and electrochemical conditions such as cathodic potential, solution chemistry, and pH level [14]. With respect to loading waveform the period during which the stress is increasing appears to have the most damaging effect on fatigue strength although the period of zero stress and the period of maximum stress can also affect strength [15]. The effect of frequency is dependent on the susceptibility of the material to SCC. According to the authors, changing stress produces delayed changes in corrosion potential which could account for the damaging effect. Other contributing factors might be damage to protective films by varying stress as well as effects on generation of slip during the rising load part of the cycle.

Because of the utility of the fracture mechanics approach considerable crack propagation data have been generated in recent years. In general, aqueous environments cause acceleration of crack propagation rate when compared with air. This effect is rather consistent in ferritic steels [16] and aluminum alloys [17], but Types 403 and 300 stainless steels [18,19] and some titanium alloys [20] are reported to be unaffected by a neutral aqueous solution. Enhancement in propagation rate can occur below as well as above K_{ISCC} . Some investigators [5,16] report that superposition models (summation of fatigue crack growth rate in inert environment and SCC rate in aggressive environment) can predict propagation rates above K_{ISCC} while others [21] report that they do not. In this regard there is uncertainty about the exact electrochemical condition at the tip of a fatigue crack so the contribution of SCC could be difficult to predict. Below K_{ISCC} the effect of environment is mainly a synergistic one between corrosion and fatigue crack propagation.

Corrosion fatigue crack propagation rate da/dN depends upon a number of variables including frequency, load waveform, K_{max} , stress ratio, ΔK , state of stress, and temperature. Generally da/dN increases with decreasing frequency and introduction of hold time. Above K_{ISCC} , at low frequency da/dN is influenced mainly by environment while at high frequency it is controlled by fatigue. Fatigue dominates da/dN also below K_{ISCC} . Generally, the environmental effect is largest at intermediate ΔK values. A reduction in frequency tends to reduce the slope and sometimes produces a step in this region of the da/dN versus ΔK curve. Atkinson and Lindley [16] found a critical frequency at which maximum attack occurred on steel in water. Barsom [22] has shown that most of the effect occurs during the rising load part of the fatigue cycle. Sensitivity to environment is decreased at high

ΔK levels and this has been attributed [23] to a reduction in degree of hydrogen embrittlement associated with the transition in fracture mode from plane strain to plane stress. Thus one would expect the effect to persist to higher ΔK levels in thicker specimens.

Observations have been made [24,25] of retardation and arrest of fatigue crack growth in steel at a very low stress intensity. This behavior has been ascribed by Paris, et al. [24] to build up of corrosion products on the fracture surfaces near the crack tip impeding crack growth according to Elber's [26] crack closure model. In this connection, in a study of fatigue of aluminum alloys, Schijve and Arkema [27] found that the environmental effect could not be explained by different amounts of crack closure. Another possible cause for the retardation is crack tip blunting. While the Paris relationship is generally used to present corrosion fatigue crack growth rate data, Hudak and Wei [28] demonstrated that under certain conditions the relationship appears not to be unique, that is several different rates may occur for a given stress intensity. Test interruptions and changes in loading variables, such as frequency, cause non-steady state crack growth and result in transient periods, the extent appears to depend upon environment.

Salt Water

Fatigue strength is generally lower in salt water and natural seawater than in air in steel, aluminum, and titanium alloys [29,30]. However, the influence of salt water relative to that of distilled water is much less clear. No difference between the effects of the two was reported in some studies while in others salt water was found to be more aggressive. In the case of 13 Cr stainless steel [31] distilled water had no influence on fatigue strength but 3% NaCl solution significantly lowered strength. Furthermore, as NaCl content was increased, fatigue life decreased. In deaerated seawater fatigue resistance was comparable to that in air [32].

Stress level or strain range may be a factor also in the response of a material to environment. For example, fatigue life of an aluminum alloy was unaffected by salt water in the low-cycle regime but it was sharply reduced in the high-cycle regime. Also high stress ratios tend to lower fatigue resistance. Another important variable is cathodic potential which can be applied to restore fatigue resistance to that in air or even improve it.

Fatigue crack propagation rates are generally increased in 3.5% salt water and seawater relative to air, the maximum effect occurring at either low [33] or intermediate ΔK levels [34-36]. Frequency and electrochemical potential strongly affect crack growth rate. Vosikovsky [34] found that at a frequency of 10 Hz the environmental effect on HY 130 steel was negligible but at 0.01 Hz the maximum increase in da/dN compared to air was 3 times at a free-corrosion potential and 10 times at a zinc potential as shown in Fig. 1. In a line-pipe steel X-65 (0.16 C, 1.34 Mn, 0.16 Si, 0.046 V, 0.031 Nb) at 0.01 Hz the maximum increase of da/dN was 10 times that of air at a free-corrosion potential and 50 times at a cathodic potential of -1.04V [35]. Furthermore [37], stress ratio strongly influenced fatigue crack growth thresholds and da/dN close to the threshold. The effect of stress ratio R was the same in salt water as in air. Vosikovsky suggested that the mechanism responsible for accelerated growth at a cathodic potential is hydrogen embrittlement and for that at a free-corrosion potential, a combination of hydrogen embrittlement and anodic dissolution.

Similar results were reported on structural steels by Scott and Silvester [38]

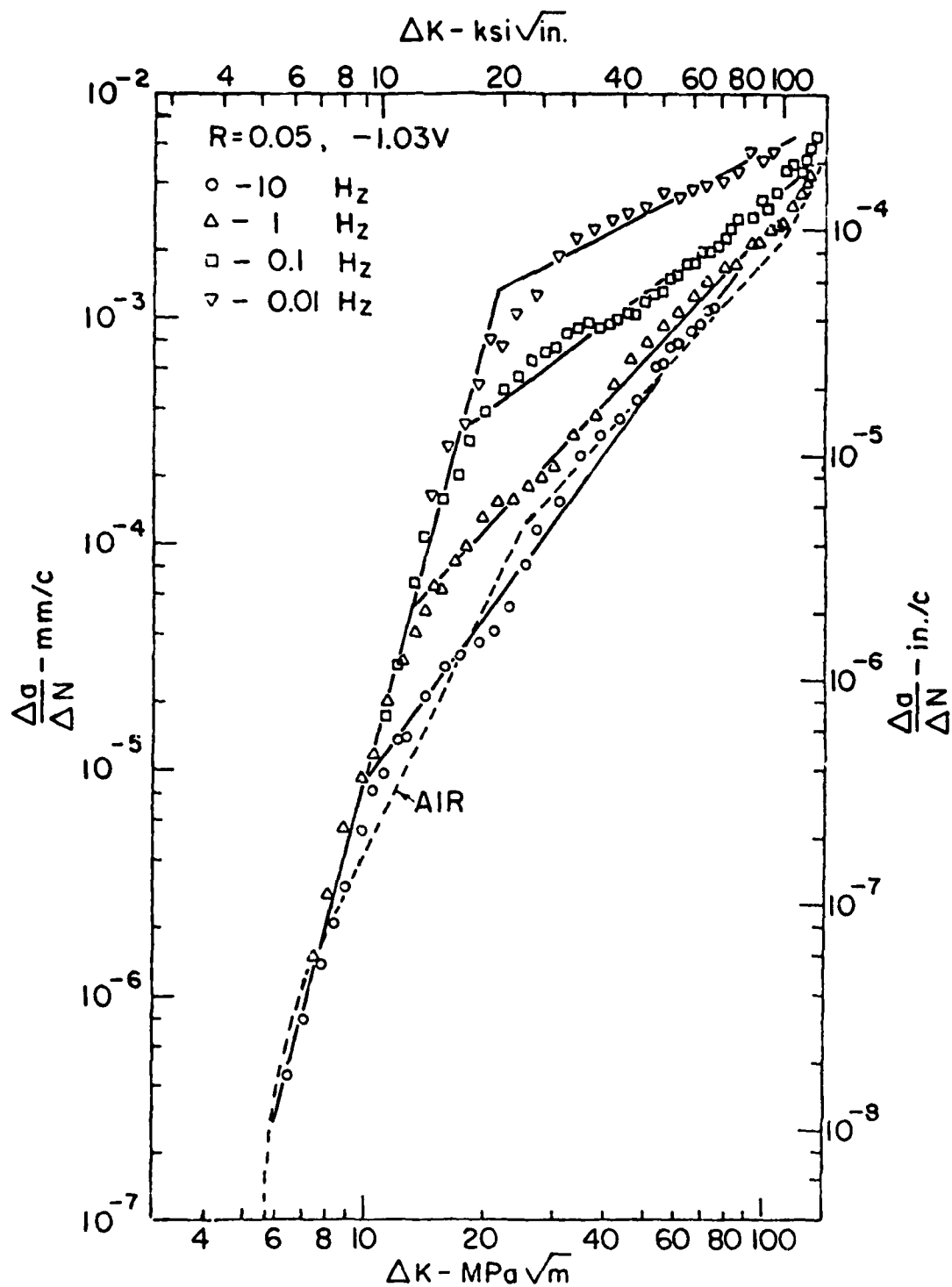


Fig. 1 — Influence of frequency on fatigue crack growth rates in HY-130 steel in 3.5% NaCl solution at zinc potential. The growth rate curve in air is for $R = 0.5$ and 10 Hz [34]. (Copyright Supply and Services Canada, 1977)

who found no significant difference between da/dN in seawater and air at a frequency of 1 Hz but at 0.1 Hz the da/dN in seawater was up to 5 times that in air. Also, potentials more negative than -0.7V generally increased da/dN . Temperature, oxygen content, and pH value had significant effects on crack growth behavior. Barsom and Novak [39] reported that da/dN in several bridge steels at 1 Hz was essentially the same for exposure in distilled water and in 3% NaCl solution. Even at 0.2 Hz, da/dN in these solutions were equal to or only slightly greater than that in air. The threshold stress intensity was greater in 3% NaCl solution than in air and the cause of this could be blunting of the crack tip by corrosion in the solution, thus requiring a higher ΔK to initiate growth. In contrast to these small environmental effects due presumably to the relatively high test frequencies, it was observed that applying alternate wet and dry environments significantly retarded da/dN . Atkinson and Lindley [16] pointed out that the environmental effect in A533 steel is primarily controlled by rise time and not total cycle time provided hold periods at K_{max} are short. Long hold times cause a reduction in da/dN in distilled water.

In tests in flowing natural seawater, Crooker, et al., [40] reported that both seawater and applied potential accelerated da/dN in the ferrous alloys (HY 130 steel, 17-4 PH) which were much more sensitive than their nonferrous alloys (Ti-6Al-2Cu-1Ta-0.8Mo and 5456-H116 aluminum), Fig. 2. In fact, the titanium alloy was not noticeably sensitive to either seawater or negative potential. While crack growth in the 5456 aluminum alloy varied widely with seawater and potential, that in 5086 alloy was only slightly affected by either even though in ambient air these two alloys exhibited similar crack growth characteristics [41]. The growth rates in the 5456-H116 alloy were significantly accelerated at the freely corroding potential but under cathodic potential the rates were retarded. In contrast to data in Fig. 2b, some other investigators [41,42] have found that salt water accelerates da/dN in both titanium and aluminum alloys. Even exposure or pre-corrosion in salt water caused a marked reduction in fatigue resistance of an aluminum alloy when subsequently fatigued in air [43]. This was attributed to hydrogen embrittlement.

Work of Krafft, et al., [44,45] has provided a model which takes into account environmental effects on fatigue crack growth rate, including as well frequency and stress ratio effects. The approach provides a way of correlating crack growth rate data with cyclic plus monotonic stress-strain properties. Briefly, the model views crack growth as a means of straining, hence strain-hardening, material within a fracture process zone. The total amount of strain hardening required derives from two sources. The primary source is viewed as stress relaxation, a consequence of a materials strain-rate sensitivity. At a given temperature, it is independent of environment. The secondary source is the environmental influence, modeled as a bit of surface attack which has the effect of surface removal, hence strength reduction due to reduction in area. The amount of surface attack in a cycle is taken as limited in one of two ways. The primary limit, as in ordinary corrosion processes, is cycle duration. Even though time is ample, the availability of nacent clean surface area, due to plastic straining of the process zone ligament, may secondarily limit surface attack. The model distinguishes cyclic from monotonic strain hardening characteristics and accounts for mean stress effects. Largely computerized, its procedures show promise of reducing the cost of fracture/fatigue life prediction of naval structures.

It is recognized that the electrolyte within a fatigue crack is an important factor in the corrosion and its chemistry could be modified with respect to the bulk electrolyte, and therefore be of an unknown character. In corrosion fatigue, as discussed by Hartt, et al., [46], the alternate opening and closing of the crack is

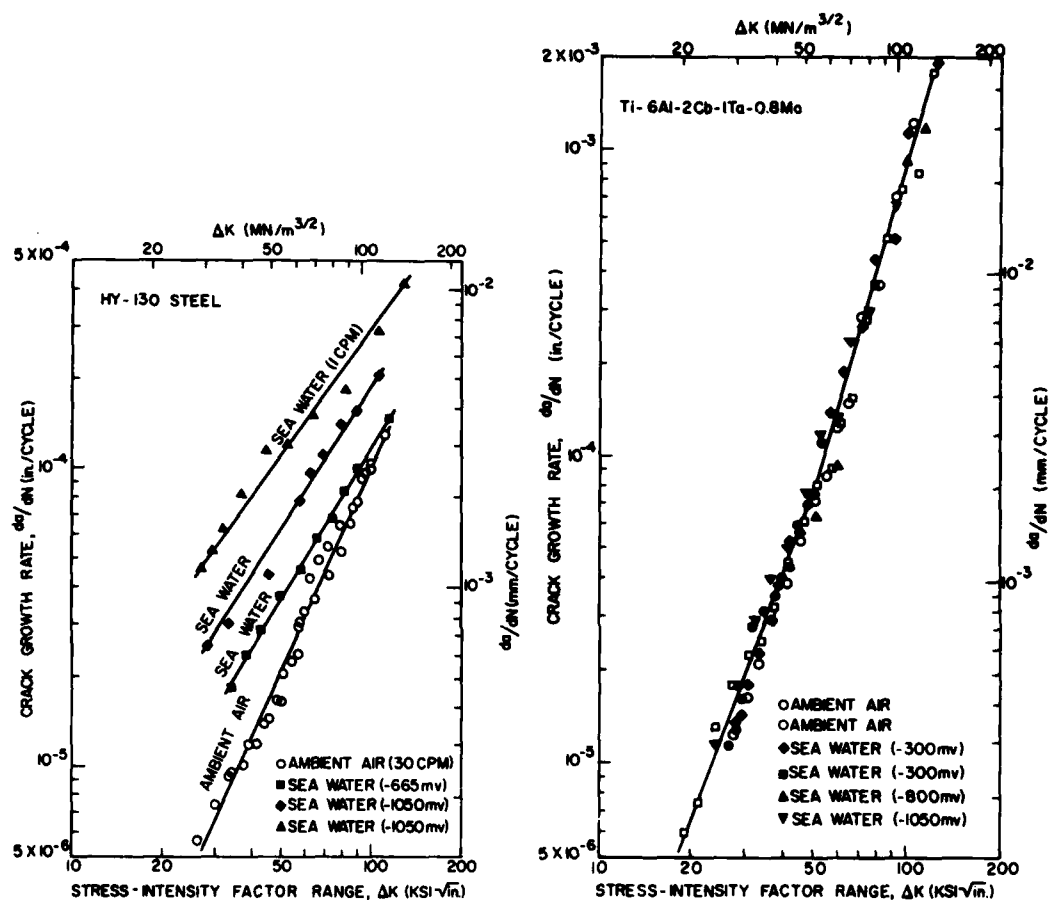


Fig. 2 — Influence of electrochemical potential on corrosion fatigue crack growth in (a) HY-130 steel and (b) Ti-6Al-2Cb-1Ta-0.8Mo alloy[40].

presumed to promote mixing of the electrolyte by pumping it in and out of the crack such that the chemistry is not changed. However, Barsom [47] noted a crack electrolyte pH of ~ 3 for a steel cycled at 0.1 Hz in 3% NaCl solution and Meyn [48] reported a pH of less than 3 for a titanium alloy at both 0.5 and 30 Hz. At low pH more hydrogen is evolved and in hydrogen-sensitive materials crack growth is enhanced. Under a cathodic potential the pH of the crack electrolyte increased. It should be noted that the crack electrolyte chemistry may differ from one specimen type to another.

Natural seawater, ASTM substitute ocean water [49], and aqueous 3.5% NaCl are often used interchangeably in corrosion fatigue studies so Bogar and Crooker [50] evaluated their relative effects on crack growth rate. They found that growth rates varied by as much as a factor of three among the three solutions. Particularly for high strength steels, natural seawater was appreciably more aggressive than either laboratory substitute, Fig. 3.

High Temperature Water

Concern about the structural integrity of water cooled nuclear reactor pressure vessels has led in the past decade to a number of fatigue investigations of reactor steels in simulated reactor water environments. It became evident early that frequency is an important factor in the response of the material to the environment. Mager and McLaughlin [51] investigated the influence of pressurized water reactor (PWR) and boiling water reactor (BWR) type coolant environments on fatigue crack growth in A533-B-1 steel at 288°C and cyclic frequencies of 1 and 10 Hz and observed no or at most only a small increase in crack growth rate. On the other hand, Kondo, et al., [52] found that da/dN in SA 302-B and SA 533-B-1 is accelerated considerably in BWR coolant at frequencies of less than 0.17 Hz. Lowering frequency from 0.17 to 0.017 Hz steadily increases da/dN but below this frequency cracks tend to incubate, reducing the average da/dN . The concentration of oxygen dissolved in the water has a strong effect on incubation time. Also crack growth rates tend to be higher at higher R ratios. Kondo, et al., [53] reported that under strain control the crack was blunted when either oxygen was increased to several ppm or when frequency was decreased to below 0.017 Hz. However, under load control, blunting did not occur. Dependence of da/dN on stress intensity increased from an exponent of 4 in air to 9 in 200 to 260°C water. Although Suzuki, et al. [54] reported a strong frequency effect on da/dN no significant effect of hold time was observed, indicating perhaps the importance of rise time. Also, microstructure strongly influences da/dN in high temperature water. Several other investigations [55,56] confirmed the acceleration of crack growth at low frequencies in a hot aqueous environment.

Bamford [57] noted the crack growth behavior of various pressure vessel steels and welds in PWR environment showed little difference and the behavior appeared to be essentially the same in both PWR and BWR environments. Increasing the mean load during the cycling, as with lowering of the frequency, increases da/dN in 288°C water [58]. The increase is pronounced at low ΔK and small crack lengths but becomes moderated at high ΔK by secondary microcracking which is a manifestation of chemical interaction at the crack tip. Here there appears to be a strong relation between test interruptions and discontinuous crack growth.

Loading waveform has been shown [59,60] to have an important effect on crack growth behavior. Whitman and Bryan [60] found the ramp time to be more important than hold time in affecting da/dN , and increasing ramp time to 1 min

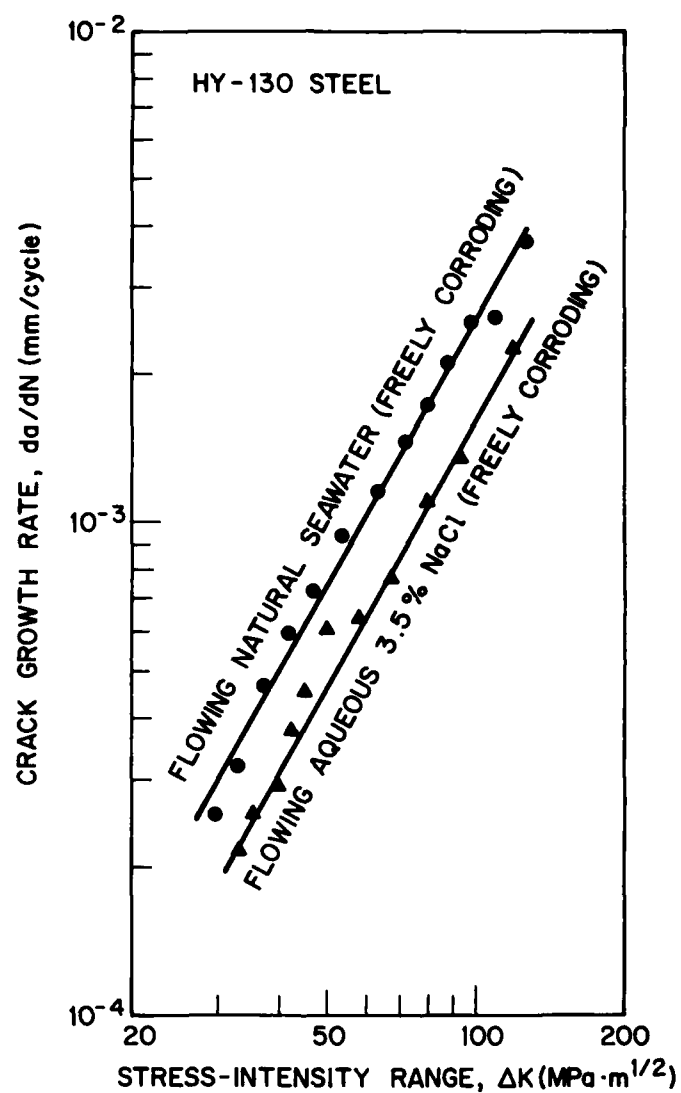


Fig. 3 — Fatigue crack growth rates for HY-130 steel in flowing natural seawater and in flowing aqueous 3.5% NaCl solution under freely corroding conditions [50].

appreciably raises da/dN . Also, Cullen, et al. [59] in a study of A508 steel in high temperature pressurized reactor grade water observed that certain combinations of waveform and temperature would put da/dN into one of two closely spaced bands. To fall in the high da/dN band a ramp time in excess of one second is needed. Inclusion of a hold period at 288°C would cause the da/dN to fall into the lower band, but under these same conditions at 93°C, the da/dN values are in the higher category, as shown in Fig. 4. It should be noted that behavior in PWR (low oxygen) environment differs from that in BWR (higher oxygen) environment in some respects.

Accelerated crack growth in high temperature water as well as in ambient temperature aqueous environments is usually attributed to hydrogen which could be generated at the crack surfaces and enters the metal to embrittle and promote crack extension through a number of possible mechanisms. These are based on hydrogen causing either hydride formation, reduction in surface energy, reduction of local stress required for dislocation motion, or increased impediment to dislocation motion affecting crack closure, among others. Sandoz [61] presented evidence showing that the effects of hydrogen on AISI 4340 were fundamentally the same whether hydrogen originates from stress corrosion, from the gas, or from electrolytic charging during or prior to testing.

GASES

Air

Air is the most commonly encountered gaseous environment in service and it has a significant effect on the fatigue failure of many alloys. The effect of air on fatigue has been determined in relation to either high vacuum or sometimes inert gas such as argon. Since air contains, in addition to the major constituents, nitrogen and oxygen, several minor constituents such as water vapor, hydrogen, CO_2 , and CO, the observed effects could be due to one or more of these gases. In many cases tests are conducted in laboratory atmosphere which over a period of time contains various levels of humidity which could in turn affect the fatigue processes to different degrees. Although it is possible, at least in some cases, to identify the most damaging constituents of air, in several cases it is difficult since, as we shall discuss later, individual gases may behave differently when they are mixed together.

The magnitude of the effect varies with the alloy under consideration. In Al-3% Mg alloy [62] air appears to affect the fatigue life but pure nitrogen alone does not. The life in air is 30% lower than in vacuum. As the pressure increases, at some critical pressure there is a sharp decrease in fatigue life and the fatigue life versus air pressure data follows a stepped curve. This type of stepped curve was found earlier in several other alloys [63-65]. The existence of a critical pressure was related to the number of gaseous atoms required to form a monolayer on the freshly created crack surface [65]. This pressure however is a function of frequency [62] and temperature [65]. Hordon [66] observed also in 1100-H14 aluminum alloy a ten-fold decrease in fatigue life in air as compared to that in vacuum. Most of this decrease in fatigue life arises from the effect of environment during the propagation stage rather than the initiation stage. Ishii and Weertman [67] have in fact observed in the same alloy a 15-fold increase in fatigue crack growth rate (da/dN) over that in vacuum, particularly at the lower stress intensity range (ΔK). At high stress intensities the difference between da/dN in air and vacuum is much less [68] suggesting that the environmental effect decreases with increase in crack growth rate.

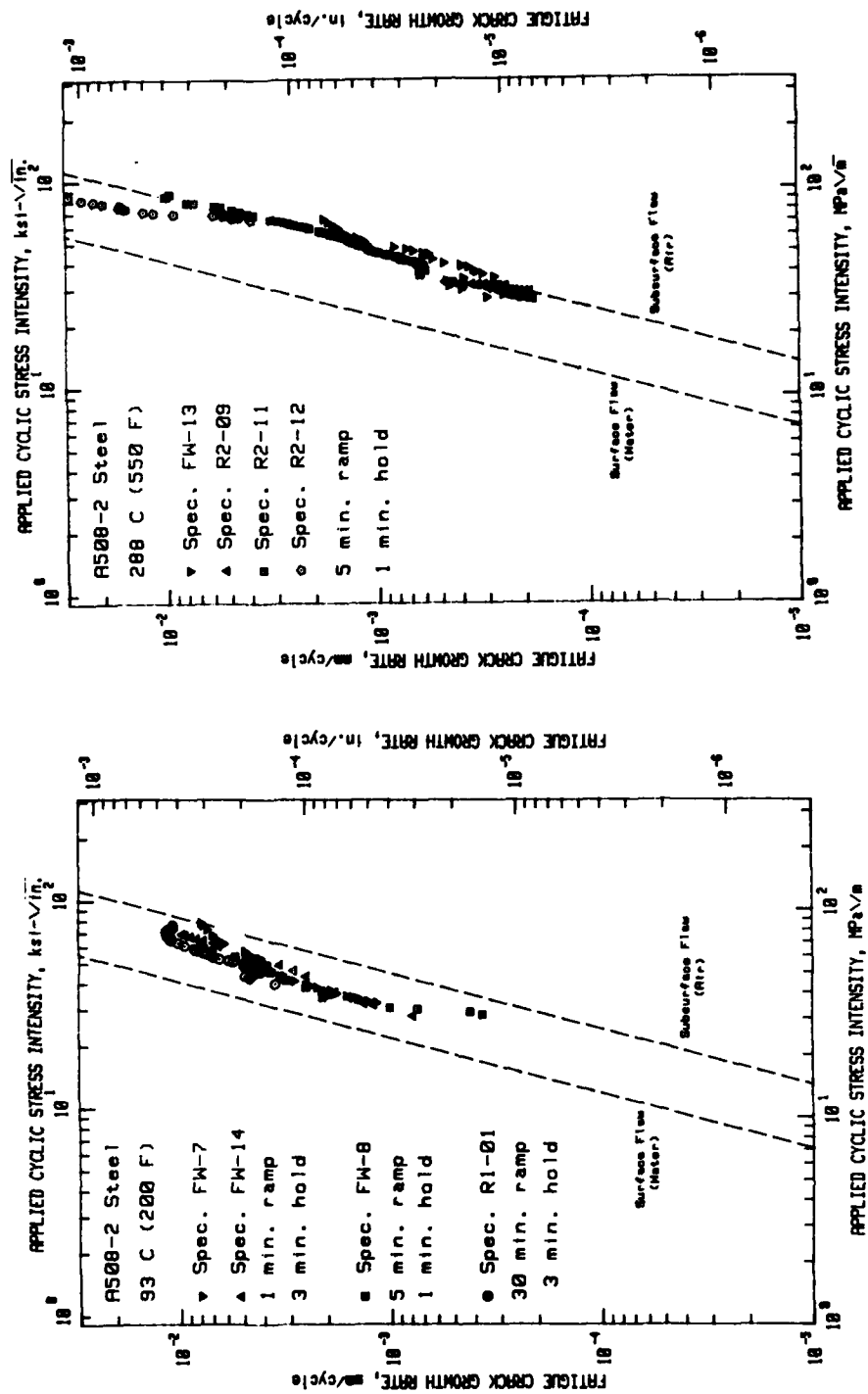


Fig. 4 — Influence of loading waveform on fatigue crack growth rates for A508-2 steel in pressurized high temperature water at 93 and 288°C [59].

There were several investigations that showed that the effect of air is more significant in the crack propagation stage of fatigue than in the crack initiation stage. The number of cycles required to initiate a crack in vacuum as compared to that in air was found to be nearly the same in several metals and alloys, such as DTD 5070A and Al-Cu-Mg alloy [69], pure aluminum [66,70], and copper [70]. On the other hand, there were a number of studies which showed that surface deformation characteristics were affected by the environment and also fewer cycles were required to initiate a crack in air than in vacuum in Al-4% Cu alloy [71], 1100-H4 aluminum [72], pure aluminum [73], 7075-T6 aluminum alloy [74], and pure lead [75]. Thus, although there appears to be a lack of agreement on the influence of air on crack initiation, there is a consensus that the environment clearly affects crack propagation more than initiation.

Bradshaw and Wheeler [69] determined the effect of air on crack growth rate in several aluminum alloys such as DTD 5070-A, SAP, and Al-Cu-Mg alloy in addition to pure aluminum. Crack growth rates in air are nearly six times greater than those in vacuum at the slow crack growth regime but this difference decreases to zero at fast crack growth rates. Similar enhancement of crack growth was also observed in other aluminum alloys such as 7075 [76] and 2024 [77].

These results are not particular to aluminum alloys alone since similar effects were observed in several steels and titanium alloys as well. For example, crack growth rate was found to be enhanced in air as compared to that in vacuum in 4340 steel [78]. More recently, Irving and Beevers [79] observed a large increase in crack growth rate in air in relation to vacuum in Ti-6Al-4V alloy. For this alloy the effect of air is pronounced in the regime where da/dN is also sensitive to the microstructure of the alloy. The transition from the structure and environment sensitive crack growth regime to structure and environment insensitive crack growth is related to the condition where the plastic zone ahead of the crack tip reaches the size of the α -grain size [79,42]. The effect of air is more pronounced in the low ΔK regime close to the threshold region and decreases with increase in crack growth rate. Wanhill [42] also reports a large increase in da/dN in air as compared to dry argon. The effect of air on fatigue crack growth was observed in several titanium alloys in addition to Ti-6Al-4V [48] such as Ti-5Al-2.5Sn and Ti-8Al-1Mo-1V [80].

In summary, crack growth rate appears to be sensitive to air environment particularly in the slow crack growth regime which is of interest for many applications. Since most fatigue studies are conducted using laboratory air, moisture is one of several important constituents which might be responsible for the observed effects. We shall discuss next to what extent the humidity level is important in accelerating fatigue crack growth.

Water Vapor

Several studies have shown that humidity in air can cause a significant effect on crack growth under fatigue. Even prior exposure [81] to humid air for 5 to 365 days before the cyclic load is applied reduced fatigue strength in several aluminum alloys such as 2024-T4, 5052-O, 5083-O, and 7075-T6. This reduction was even more when humid air was admitted into the vacuum chamber during the test.

Bradshaw and Wheeler [69] investigated the effect of humidity on crack growth in several aluminum alloys; DTD 5070A, SAP, and pure Al, and found as much as a tenfold increase in crack growth rate due to water vapor. There was a

stepped increase in crack growth rate with increase in the partial pressure of water vapor, humid air, or humid nitrogen. Studies on 7075 Al alloy [76] also showed that crack growth rates in laboratory air and wet argon are higher than in dry argon. On the other hand, dry oxygen has a small effect on crack growth rate in the alloy. Enochs and Devereux [82] also observed a critical pressure at which the effect of water vapor reaches a plateau in 5052 Al alloy. They found that this critical pressure decreases with increasing R. George [83] observed a similar increase in crack growth in humid air in L65 age hardenable alloy.

The effects of humidity are again not specific to aluminum alloys since similar effects were observed in steels as well as in titanium alloys. Acceleration of fatigue crack growth in the presence of humidity was observed [84,85] in 4340 steel. Also Wei, et al., [86] observed that crack growth rate in a 18 Ni maraging steel increased with increase in humidity in an otherwise inert environment such as argon. They also observed that humidity greater than 40% RH has no additional effect on crack growth. This is similar to the observation of a plateau with increase in partial pressure. From the several alloys tested with varying yield strengths it was shown that the effect of humidity becomes more pronounced with increase in yield strength or more particularly with decrease in fracture toughness. Johnson and Paris [87] have discussed that the humidity effects in steels are of concern mostly for alloys with yield strengths greater than 1240 MPa. Similar to steels, titanium alloys such as Ti-6Al-4V and Ti-6Al-6V-2Sn also show a decrease in fatigue life with increase in relative humidity [88]. Humidity seems to affect crack growth rates even in austenitic stainless steel [89,90].

It is clear from the above observations that water vapor is a very important and in most cases an unavoidable element of the environment which significantly affects fatigue crack propagation and thus the fatigue life of several structural materials including Al and Ti alloys as well as high strength steels. In many cases the effect of water vapor may not be solely due to the direct effect of water molecules but could be due to the hydrogen atoms liberated during disassociation of water molecules at freshly created metal surfaces. To understand the effect of humidity it is necessary to examine the effect of hydrogen on fatigue failure.

Hydrogen

Hydrogen in solution is known to cause embrittlement under monotonic or static loads. There appears to be some consensus that in many alloy systems, the effects of internal and external hydrogen are similar or related. In fact, there is a general feeling [61] that cracking due to stress corrosion in an aqueous medium, to hydrogen gas, or due to charged hydrogen are all similar and any differences in the kinetics of the embrittlement are due to differences in the kinetics of the supply of atomic hydrogen at or near the crack tip region. Again, hydrogen appears to have a significant effect on fatigue crack growth in aluminum alloys, steels, and titanium alloys.

Broom and Nicholson [71] have shown that the fatigue life in hydrogen is reduced to nearly one-third of that in air for Al-4%Cu and BS L65 alloys. In Armco iron and in several ferrous alloys (both ferritic and austenitic steels), Romaniv, et al., [91] showed fatigue life decreases sharply in the presence of hydrogen gas. This detrimental effect of hydrogen is a maximum at or near room temperature and decreases to zero with increase in temperature to 200 to 250°C. Also the effect was found to be independent of the crystallography of the alloy (fcc or bcc). Clark [92] observed in HY-80 steel that fatigue crack growth rate increases in dry

hydrogen by a factor of 10 to 30 over that in laboratory air, depending on the ΔK value. But the effect is less (only three times) in HY-130 steel although its yield strength is higher than that of HY-80 steel. In general, however, susceptibility of a material to hydrogen attack increases with the increase of its yield strength. This is shown more clearly in Fig. 5 where threshold stress intensity for crack growth in AISI 4340 steel in different hydrogen producing environments is represented as a function of its yield strength. Frandsen, et al., [93] also observed similar effects in HY-80, A514-B and HP 9-4-20 steels. Enhanced crack growth in gaseous hydrogen was observed in several other steels such as ASME SA 105 Grade II steel by Walter and Chandler [94], D6AC steel by Ryan [95], and in 18 Ni maraging steel by Spitzig, et al., [96]. Medium carbon steels also behaved similarly in the presence of gaseous hydrogen. In particular Prowse and Wayman [97] have found that crack growth rates in medium carbon steels are higher in dry hydrogen than in dry argon, humid argon or humid hydrogen. Karpenko, et al., [98] have found that martensitic steels are much more susceptible to hydrogen effects than ferritic and austenitic steels. It is not clear whether it is related to the microstructure per se or to their higher strength.

Hydrogen was found to affect crack growth and fatigue life in titanium alloys as well. Fatigue life was shown to be lower in Ti-Al-Zr alloy [99] in the presence of gaseous hydrogen. Pittinato [100] has reported that hydrogen markedly accelerates fatigue crack growth in equiaxed Ti-6Al-4V alloy at temperatures below 0°F. As in air [79], the effects are sensitive to ΔK values and microstructure of the alloy.

In recent years the influence of test temperature on the effects of hydrogen has received much attention. The approach was to identify the mechanisms of the environmental effect using activation energy measurements. Several investigations [91,93,101] have found that hydrogen effects on fatigue reach a maximum at or near room temperature and decrease with decrease or increase of temperature as shown in Fig. 6. The results are similar to the hydrogen effects observed under static load [102]. In fact, Nelson, et al., [102] showed that crack growth rate under static load depends on the nature of hydrogen gas, that is, whether it is in molecular form or in atomic form. They found that the crack growth rates are significantly higher and the temperature dependence is different when the tests are conducted in partially dissociated hydrogen as compared to molecular hydrogen gas. The authors attribute the difference to change in the rate controlling process from that of dissociation for molecular hydrogen to formation of solid solution for atomic hydrogen. Activation energy in one case corresponds to dissociation energy and in the other case to heat of solution. It is presumed that similar differences could arise even under fatigue.

The critical pressure of hydrogen required for enhancement of fatigue crack growth in a high strength steel was reported by Stegman and Shahinian [103] to be higher than that of either water vapor or oxygen by a factor of over 100. In addition, unlike in oxygen and water vapor, crack growth rate increased continuously with increase in pressure without reaching a plateau, indicating the absence of any saturation effect. The high pressure required indicates that the rate-controlling mechanism of the hydrogen effect is not gas adsorption. In contrast, the critical pressures of water vapor and oxygen agree well with the predictions of the adsorption model.

Thus among all commonly encountered gases, hydrogen appears to have the most detrimental effect on crack growth behavior. The magnitude of the hydrogen effect is sensitive to the source of hydrogen, the partial pressure of hydrogen, frequency of cycling, and magnitude of the stress amplitude in addition to test

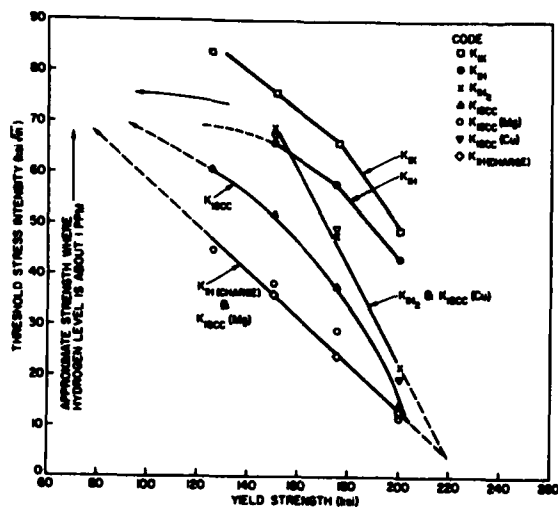


Fig. 5 — Effect of yield strength on threshold stress intensities for crack growth in AISI 4340 steel [61].

Parameter	Definition
$K_{I\alpha}$	An approximation of K_{Ic} . (Specimen step-loaded in air 5 ksi $\sqrt{\text{in.}}$ per min.)
K_{IH}	Similar to $K_{I\alpha}$ but loaded slowly (≈ 5 ksi $\sqrt{\text{in.}}$ per hr).
K_{IH_1}	Threshold stress intensity in gaseous hydrogen.
K_{Icc}	Threshold stress intensity (maximum stress intensity without crack growth for 100 hr) with 3.5 pct NaCl—freely corroding.
$K_{Icc}(\text{Mg})$	Same as K_{Icc} but with the specimen coupled to a magnesium anode (steel cathodically polarized).
$K_{Icc}(\text{Cu})$	Same as K_{Icc} but with the specimen attached to a copper cathode (steel anodically polarized).
$K_{IH}(\text{charge})$	Threshold stress intensity in air after electrolytic charging to "saturation" (attached to a magnesium anode and submerged in 3.5 pct NaCl solution saturated with H_2S for at least 24 hr).

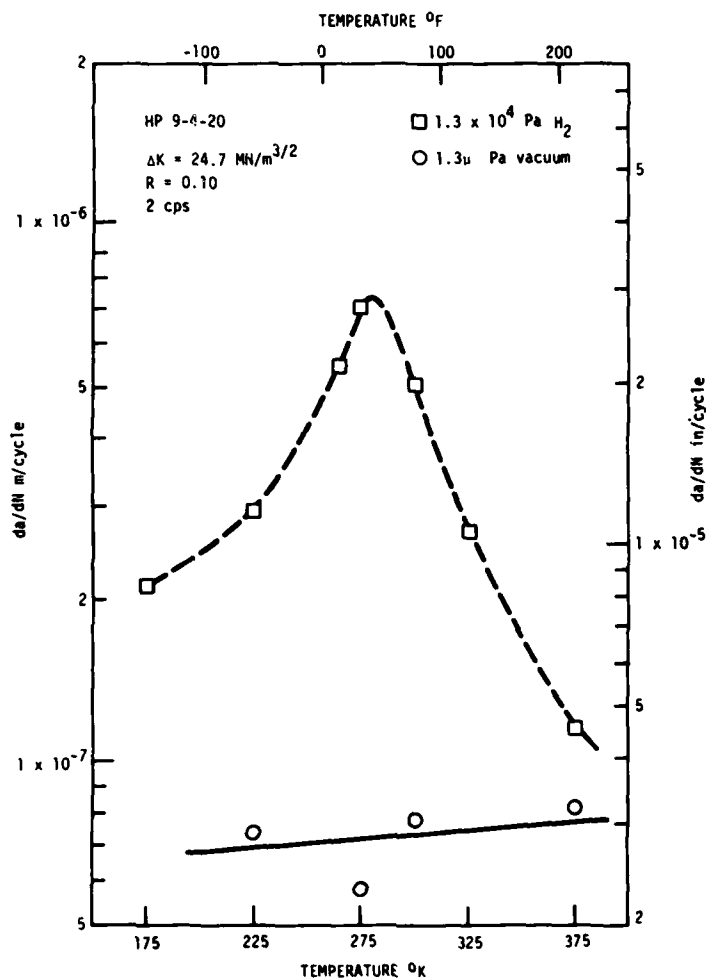


Fig. 6 — Temperature dependence of hydrogen effect on fatigue crack growth in HP-9-4-20 steel [93]. (Copyright American Society for Metals and The Metallurgical Society of AIME 1976)

temperature and microstructure of the alloy. In addition to these variables the effect of hydrogen is influenced by the presence of other gases and these aspects will be discussed next as well as the effects of the individual gases.

Other Gases

Effects of other gases such as oxygen, nitrogen, carbon monoxide, carbon dioxide, acetylene, methane, nitrous oxide, and combinations of these with hydrogen have been studied. For ASTM 514-B alloy, HY-80 and HP 9-4-20, Frandsen and Marcus [93] have shown that fatigue crack growth rate increases in various amounts for different alloys and different gas combinations. In general, hydrogen is the most damaging. The other gases such as oxygen, CH_4 , CO , CO_2 , and N_2O are less effective individually. When hydrogen is combined with O_2 , CO , N_2O , or H_2O , the effect is less than what might be expected on the basis of the linear summation of the effects due to the individual gases. These synergistic effects have been attributed to preferential adsorption of O_2 , CO , N_2O , or H_2O on crack surfaces.

The effect of air on fatigue has been found to be largely due, in addition to water vapor, to oxygen. Crack growth rate in pure aluminum is significantly increased in oxygen whereas in several aluminum alloys, the increase in rate is much less and occurs usually at low stress intensities [69]. However, oxygen is clearly less aggressive than water vapor to aluminum. In a high strength steel [103] oxygen had about the same effect on crack growth rate as water vapor and also the critical pressure at which the rate increased was the same for both gases as shown in Fig. 7. However, for combinations of the two gases the effects were not additive. Smith and Shahinian [104] showed that while oxygen as well as water vapor reduces the fatigue life of nickel at 300°C the effect of the oxygen is significantly larger as shown in Fig. 8. Also, the variation of life with pressure differs for the two gases, oxygen gives a step curve whereas water vapor gives a continuous gradual change. It is also of interest to note [105] that surface slip markings produced by cyclic loading on Inconel X-750 at 500°C are quite different in oxygen and in vacuum, and as a result crack initiation occurs much earlier in oxygen.

Other gases also were found to have an effect on fatigue failure. Prowse and Wayman [97] have observed that H_2S decreases the fatigue life in medium carbon steels to the same extent as hydrogen gas. On the other hand, Ebara, et al. [106] observed that dry SO_2 has no effect on fatigue strength of mild steel, high strength steels, and 18-8 stainless steel but when humidity is added to SO_2 gas there is a decrease in fatigue strength and this decrease is the same as in humid air. Wanhill [42] found that crack growth in titanium alloys increased in the order, dry argon, normal air, distilled water and aqueous 3.5% NaCl solution, as shown in Fig. 9. The effect could be due to increasing amounts of hydrogen available at the crack tip in each environment. Purushothaman, et al., [107,108] also observed that oxygen increases crack growth rate in Monel K-500 but not to the same extent as hydrogen.

SUMMARY

The effects of aqueous solutions and environmental gases on fatigue crack nucleation and propagation in steels, aluminum alloys, and titanium alloys were reviewed. Crack nucleation is rather insensitive to gaseous environments in comparison to crack propagation but it is clearly sensitive to aqueous solutions. Much attention during the past decade was centered on the crack propagation stage. Although fracture mechanics techniques have provided a convenient means of analysis of the effects of environment on crack growth behavior, understanding of

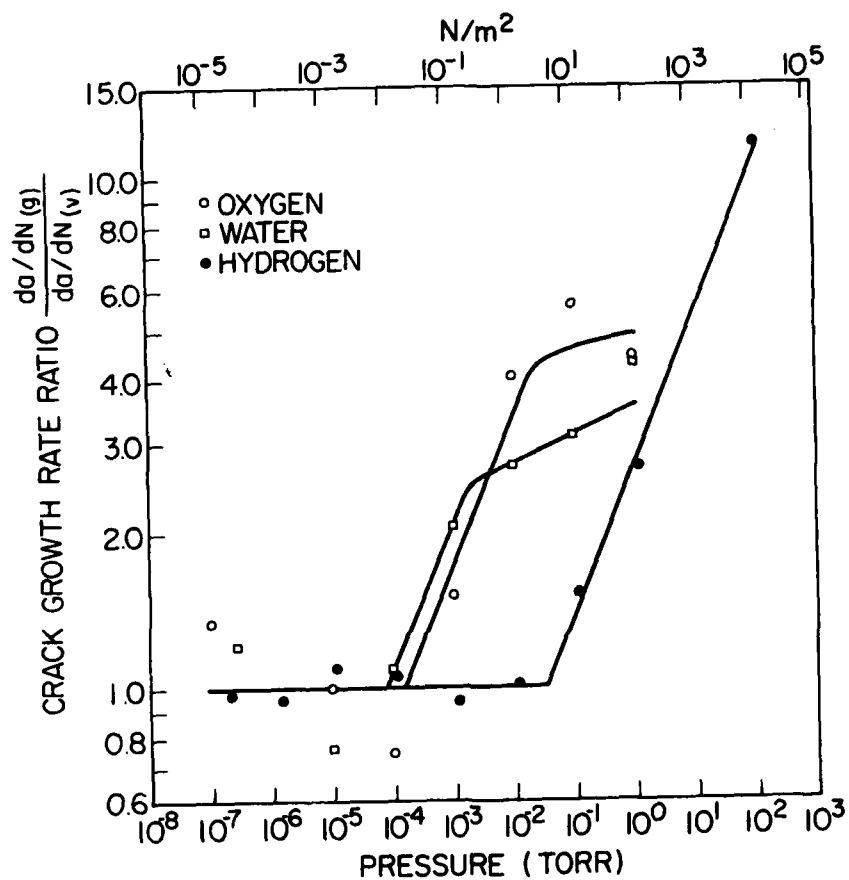


Fig. 7 — Pressure-dependence of fatigue crack growth rate in H-11 steel at 20°C and 0.108% strain in oxygen, water vapor, and hydrogen [103].

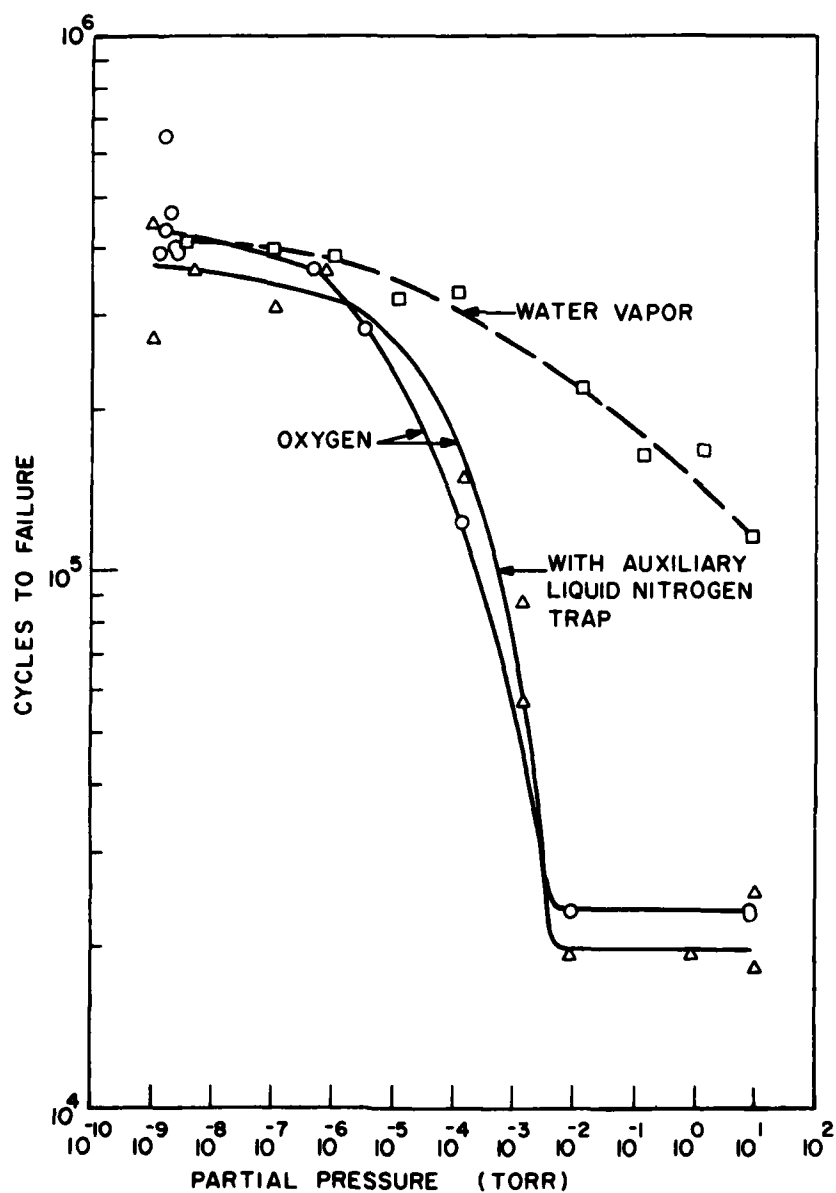


Fig. 8 — Effect of oxygen and water vapor pressure on fatigue life of nickel at 300°C at plastic bending strain of 0.17% [104].

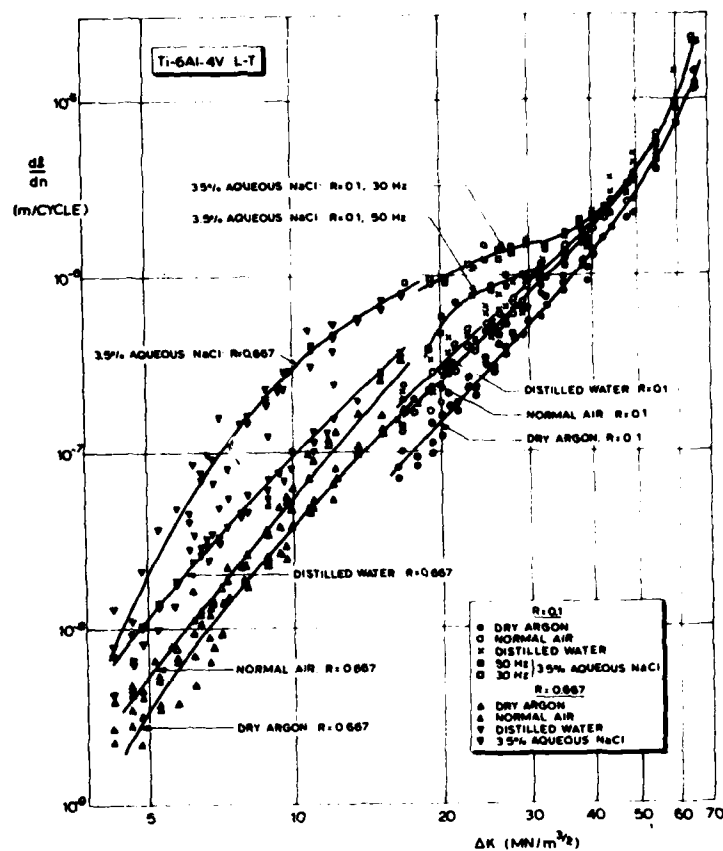


Fig. 9 — Influence of environment on crack propagation in Ti-6Al-4V alloy [42].
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these effects is far from complete. Nevertheless, efforts are underway to incorporate environmental effects into design codes.

Fatigue crack propagation is generally enhanced by aqueous solutions, particularly seawater, and by reactive gases, notably hydrogen, water vapor, and oxygen; the extent varies appreciably according to the specific metal-environment system. The magnitude of the effects depends upon temperature, frequency, waveform, ΔK , strain range, stress ratio, alloy microstructure and strength, and chemistry of the environment and material. In addition to the above factors, in aqueous solutions the electrochemical potential and pH of the electrolyte in the crack are important and in gaseous environments the partial pressure of the gaseous species can govern behavior.

Fatigue crack growth in aqueous environments is often described according to whether it is above or below K_{ISCC} . Above K_{ISCC} , stress corrosion cracking dominates at low frequencies and fatigue dominates at high frequencies while below K_{ISCC} the fatigue process governs but may be enhanced by the environment. Generally aqueous environments in comparison to air cause acceleration of crack growth at low frequencies but not at high frequencies, the high strength steels being more sensitive than nonferrous alloys particularly in salt water. With respect to the electrochemical conditions the effect is greater with more negative potential, and the accelerated crack growth is usually attributed to hydrogen.

In high temperature pressurized water, fatigue crack growth is accelerated at frequencies of 0.17 Hz and lower but is largely unaffected at 1 Hz and above. Also, increasing the ramp time during the loading cycle raises the growth rate whereas hold time appears to be less important.

In contrast to liquids, pressure is an important variable for gases which determines the number of gas molecules available for reaction at the gas-metal interface and thus this has been the subject of several studies. In terms of the partial pressure of the gas there appears to be a saturation effect in many systems that could be related to the critical concentration required to form a monolayer of gas atoms over the freshly created crack surfaces. Consequently, in aggressive environments, fatigue life and crack growth rate for many materials follow a stepped curve in terms of gas pressure. However, some materials show a continuous variation of growth rate with pressure but it is possible that the effect of the gas could reach a plateau at still higher or lower pressures than those studied.

Among the more common gases, hydrogen and hydrogen containing gases appear to be the most damaging relative to vacuum, and the effect of hydrogen is more when it is alone than when it is with other gases. Furthermore, this effect appears to be a maximum at or near room temperature and is essentially absent at temperatures greater than about 200°C in ferrous alloys. On the other hand, oxygen and nitrogen would have an increasing effect with rise in temperature.

In addition to the above, certain generalities in behavior with only an occasional exception are apparent as cited here:

- a. Fatigue life is lower and crack growth rate is higher in an aggressive environment (water, hydrogen, oxygen, air, etc.) than in an inert one (vacuum, argon).

- b. Environmental effects on fatigue are larger at lower frequencies and lower strains and stress intensities.
- c. Susceptibility to hydrogen effect increases with higher strength.
- d. Stress waveform is important in environmental effects and the rise time component appears to be particularly so.
- e. Effects of aqueous environments including water vapor on crack growth in steels, aluminum alloys and titanium alloys are generally attributed to hydrogen generation and diffusion which tends to embrittle the material.
- f. Fatigue strength is lower in salt water than in air.

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